

Direct Observation of Benzene and Pyridine Molecules Adsorbed in Microporous Carbon using Soft X-ray Emission Spectroscopy

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INTRODUCTION

Microporous carbon has been studied for a long time as a prototype of microporous materials and it is also widely used for adsorbent of organic compounds in many industrial fields. However, organic molecules in microporous carbon have seldom been directly observed, and their electronic structures and chemical bonding states in the micropores are not clearly understood. In order to directly observe molecular adsorbates in microporous materials, one needs to use spectroscopic methods that have bulk-sensitivity, high-resolution, and high-efficiency. One suitable method is soft x-ray emission spectroscopy using highly brilliant synchrotron radiation [1], because of the longer transmission length of soft x-rays in solid matter. It can also analyze both conducting and insulating materials, because the x-ray emission process is not affected by the electrical charge of the target materials. The aim of our work is therefore to directly observe organic molecular adsorbates in microporous carbon using soft x-ray emission spectroscopy, and to determine their electronic structures and chemical bonding states. In this paper, we report unprecedented examples of in situ direct observations of adsorbate benzene and pyridine molecules, which are regarded as significant pollutants in environmental molecular science, in microporous carbon.

EXPERIMENT

Benzene- and pyridine-adsorbed microporous carbon samples were prepared by covering commercially obtained activated carbon powders (100 mesh, Darco^R, G-60) with benzene and pyridine (solvents), respectively, and then drying them at room temperature. C K X-ray emission spectra were measured using a grating x-ray spectrometer installed in beamline BL 8.0. The experimental details were described elsewhere [2].

RESULTS AND DISCUSSION

Figure 1 shows the C K x-ray emission spectra of the benzene-adsorbed microporous carbon system. The upper panel shows the C K x-ray emission spectra of (A) benzene-adsorbed microporous carbon and (B) untreated microporous carbon, which were normalized at the background intensity observed in the energy region higher than 285 eV. The spectral features of the untreated microporous carbon, which consisted of a main peak near 278 eV with a low-energy tail and a high-energy shoulder near 282 eV, are in good agreement of those of graphite powder. This shows that the local molecular structure of the microporous carbon is similar to that of graphite. The maximum peak intensity of the benzene-adsorbed microporous carbon was more than 360,000 counts, and the S/N ratio seemed to be sufficient to obtain the x-ray spectrum of benzene molecules adsorbed in the microporous carbon, as described later. Little difference was observed in the spectral features of the benzene-adsorbed microporous carbon and the untreated microporous carbon. This shows that the concentration of adsorbate benzene molecules in the microporous carbon may be on the order of a few percent: the area ratio $[(A)-(B)] / (B)$ was about 8 % here. To obtain the x-ray emission spectrum arising from the adsorbate benzene molecules in the microporous carbon, we subtracted the spectrum of the untreated microporous carbon from that of benzene-adsorbed microporous carbon. The remaining spectrum (A)-(B) is shown in the lower panel. It has a sharp main peak at 278 eV with a low-energy tail and a high-energy peak at 283 eV. Superimposed on it is the calculated C2p density of states (DOS) spectrum of a benzene molecule broadened with 0.5-eV-FWHM (full width at half maximum) Lorentzian functions. This C2p-DOS spectrum was obtained by discrete variational (DV)-Xa molecular orbital calculation [3]. Major peaks in this spectrum are denoted by *a* to *g* in the figure. The spectral features of this calculated C2p-DOS are in good agreement with those of the C K x-ray emission spectrum of benzene molecules published elsewhere [4]. Comparison of the subtracted x-ray spectrum (A)-(B) with the calculated C2p-DOS spectrum shows that the spectral features of the

x-ray spectrum are similar to those of the calculated spectrum; the high-energy peak at 283 eV corresponds to peak *a* in the calculated spectrum, the main peak at 278 eV to *b* and *c*, and the low-energy tail to *d* to *g*. Therefore, the subtracted x-ray spectrum (A)-(B) is probably due to the adsorbate benzene molecules. This also demonstrates the feasibility of direct observation of benzene molecules adsorbed in microporous carbon by soft x-ray emission spectroscopy. However, some fine differences in spectral shape were observed between the subtracted x-ray spectrum (A)-(B) and the calculated C2p-DOS spectrum of a benzene molecule; for example, the peak intensity ratio among the peaks *a* to *c*. These may be caused by the electronic interaction of the benzene molecules with the surfaces of the micropores in the microporous carbon. Therefore, they should provide information about the electronic structure and chemical bonding state of the adsorbate benzene molecules in micropores.

Figure 2 shows the C K x-ray emission spectra of the pyridine-adsorbed microporous carbon system. The upper panel shows the C K x-ray emission spectra of (A) pyridine-adsorbed microporous carbon and (B) untreated microporous carbon, which is the same spectrum as in Figure 1. The lower panel shows the spectrum remaining after subtracting (B) from (A), which should provide the x-ray spectrum of the adsorbate pyridine molecules in the microporous carbon. The subtracted x-ray spectrum (A)-(B) has a main peak at 279 eV with a high-energy shoulder near 284 eV, a low-energy shoulder near 276 eV, and a low-energy tail from 275 to 265 eV. Superimposed on it is the calculated C2p-DOS spectrum of a pyridine molecule broadened with 0.5-eV-FWHM Lorentzian functions. Major peaks in the calculated C2p-DOS spectrum are denoted by *a'* to *g'* in the figure. Comparison of the subtracted x-ray spectrum (A)-(B) with the calculated C2p-DOS spectrum shows that spectral features of the x-ray spectrum are similar to those of the calculated spectrum: the high-energy peak near 284 eV corresponds to peak *a'* in the calculated spectrum, the main peak at 279 eV to *b'*, the low-energy shoulder near 276 eV to *c'* and *d'*, and the low-energy tail to *e'* to *g'*. Therefore, the subtracted x-ray spectrum (A)-(B) is probably due to the adsorbate pyridine molecules. In addition, its spectral features are clearly different from those in the benzene-adsorbed system, even though the same untreated microporous carbon spectrum was used for both systems. This difference is also strong evidence of the direct observation of adsorbate molecules in the microporous porous carbon.

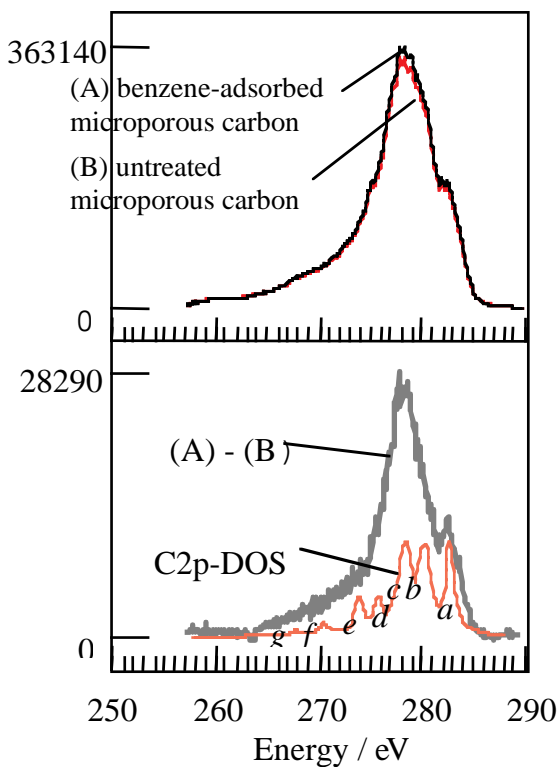


Figure 1 C K X-ray emission spectra of benzene-adsorbed microporous carbon.

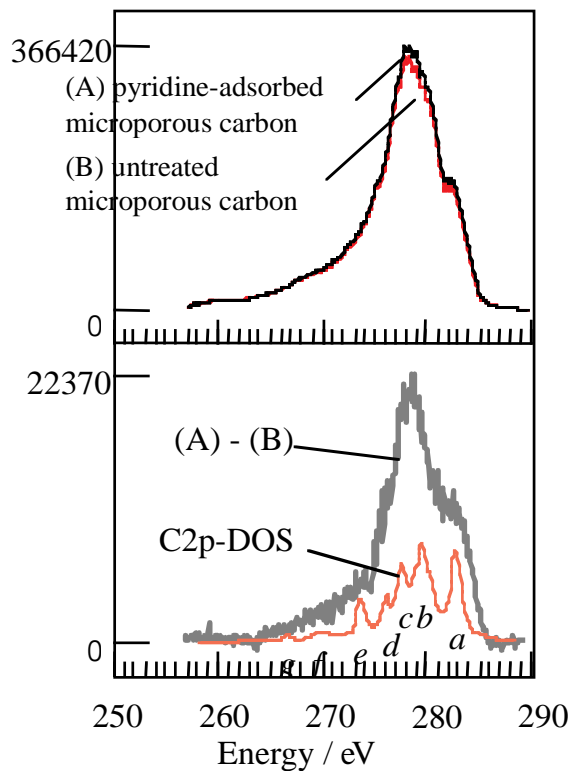


Figure 2 C K X-ray emission spectra of pyridine-adsorbed microporous carbon.

The fine spectral-shape-differences between the x-ray spectrum of the adsorbate pyridine molecules and the calculated spectrum may be caused by the electronic interaction of the pyridine molecules with the surfaces of the micropores in the microporous carbon. We will therefore try to obtain information about the electronic structure and chemical bonding state of the adsorbate pyridine molecules in the microporous carbon from further theoretical analysis of the x-ray emission spectra.

CONCLUSION

In conclusion, we successfully measured C K x-ray emission spectra of benzene- and pyridine-adsorbed microporous carbon in order to directly observe these aromatic molecular adsorbates and identify their electronic structures and chemical bonding states in micropores of the microporous carbon. We observed spectral feature differences in C K x-ray emission between the adsorbate benzene and pyridine molecules, and the x-ray spectra agreed closely with their corresponding calculated C2p-DOS spectra. Further theoretical analysis of these x-ray spectra is in progress to reveal the interaction of individual molecular adsorbates with the surfaces of micropores in the microporous carbon. We therefore believe that synchrotron-radiation- excited soft x-ray emission spectroscopy is a powerful tool for investigating molecular adsorbates in porous materials.

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REFERENCES

- [1] For example, J. Nordgren, *New Direction in Research with Third-Generation Soft X-Ray Synchrotron Radiation Sources* Ed. by A. S. Schlachter and F. J. Wuilleumier (Kluwer Academic Publishers, 1994), pp. 189.; D. L. Ederer, K. E. Miyano, W. L. O'Brien, T. A. Callcott, Q.-Y. Dong, J. J. Jia, D. R. Mueller, J. -E. Rubensson, R. C. C. Perera, and R. Shuker, *ibid.* , pp. 281.
- [2] Y. Ueno and Y. Muramatsu, *Carbon*, to be published.
- [3] H. Adachi, M. Tsukada, and C. Satoko, *J. Phys. Soc. Jpn.*, 45, 875 (1978).
- [4] P. Skytt, J. Guo, N. Wassdahl, and J. Nordgren, *Phys. Rev. A*, 52, 3572 (1995).

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